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REPLY TO OFFICE COMMUNICATION OF JANUARY 25, 2011

In reply to the Office Communication of January 25, 2011, Applicant submits a copy of the following references as requested:

Klaer et al., "Optimization of the Microstructure of Cemented Carbide Grades for Hot Rolling Applications", P/M Science & Technology Briefs, vol. 1, no. 4, (1999), pp 5-9; and

K. Tsubouchi et al., "Development of a wear-resistant surface layer for a tool to be used for high-temperature stainless steel rolling", Proc. Instn. Mech. Engrs., vol. 213 Part J (1999), pp 473-480.

A prompt and favorable office action on the merits is respectfully requested.

Respectfully submitted,

Date: February 16, 2011

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OPTIMIZATION OF THE MICROSTRUCTURE OF CEMENTED CARBIDE GRADES FOR HOT ROLLING APPLICATIONS

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ABSTRACT

Coarse grained Cemented Carbides are commonly used for hot rolling applications. In these applications the main loadings are wear and thermoshock, causing propagating cracks. In this paper theoretical considerations using FEM lead to the following conclusion: The crack propagation speed in structures with rounded WC-crystals is reduced compared to structures with normal triangle and trapezoidal shaped WC grains. These optimized microstructures were realized in mixed binder Cemented Carbide grades by using special raw materials and production conditions. These new grades are running in promising field tests.

INTRODUCTION

Production of wire rod and light sections is accomplished by passing hot billets through the stands of a rolling mill as illustrated in Figure 1. The process begins by feeding the billet through the driven rolls (also called rings) at the entrance of the mill. As the billet travels through the mill, pairs of grooved rolls in each stand plastically deform it to the desired shape.

As the billet is compressed and elongated between the rolls high tension and compressive forces are generated within the roll. In addition relative sliding between the roll surface and the billet gives rise to abrasive wear. When the hot billet material contacts the roll a temperature spike occurs in a small volume near the roll surface. The resultant thermal gradient leads to high stresses in this volume. The rolls must be cooled with water to prevent excessive heat build up in the contact zone and a subsequent rapid deterioration of the mechanical properties of the hardmetal. This gives rise to thermal cycling at the roll surface and causes a pattern of microcracks to form owing to the differential thermal expansion of the WC and Co phases. These cracks grow via thermal fatigue resulting in a network of cracks that looks like orange peel or snake skin as illustrated in Figure 2a.

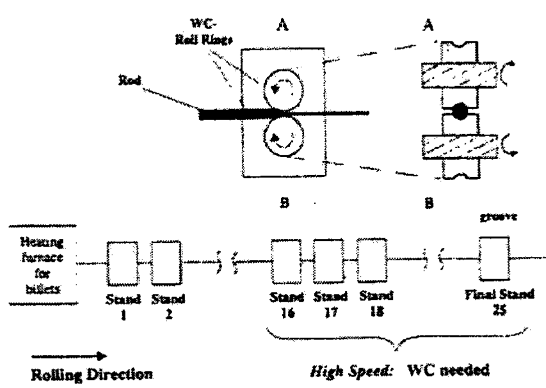
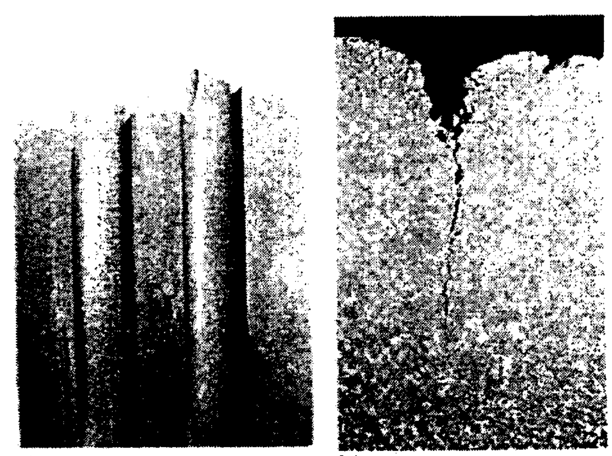


Figure 1. The Rolling Process



a) b)

Figure 2.
a) Orange peel in a worn groove caused by thermal shock
b) Deep crack in a groove of roll a roll ring

If any crack reaches the critical length under the applied rolling stress catastrophic failure of the roll can occur. Figure 2b show examples of deep cracks that can lead to catastrophic roll failure. The aim of this work is to describe a new development in the optimization of hardmetal grades with mixed binders that meet the special thermo-mechanical loading conditions of the hot rolling process.

OPTIMIZATION STRATEGY

According to the above considerations the criteria for hardmetal rings used for hot rolling is adequate abrasive wear resistance coupled with a slow rate of crack propagation. At a given binder phase concentration the crack propagation speed decrease with increasing WC grain size [1]. Crack propagation under cyclic thermo-mechanical loading conditions is primarily through the binder phase and along the WC/binder interface [2, 3]. Hence the crack propagation speed is influenced by the mechanical properties of the binder phase, the WC binder interface and the local stresses in the material. Experience shows that the structure of hardmetal grades with straight Co binders differs a little from those with mixed binders (Figure 3).

In hardmetal grades with straight Co binders the WC grains typically have triangular or trapezoidal shapes as illustrated in Figure 3a. In contrast, WC grain morphology in mixed binder grades tends to be more rounded as shown in Figure 3b. This difference is due to the solution-precipitation grain growth mechanism that predominates during the liquid phase sintering of the two types of hardmetals.

This rounded WC structure should resist crack propagation better than the sharper structure as the following numerical simulation in Figure 4 shows. Here all stresses are normalized to the highest stress in Figure 4b. Both structures are loaded in x-and y-direction with $e_x = e_y$. The volume percentage of WC and binder are the same in both examples. The physical values for the single phases are taken from the literature [4, 5].

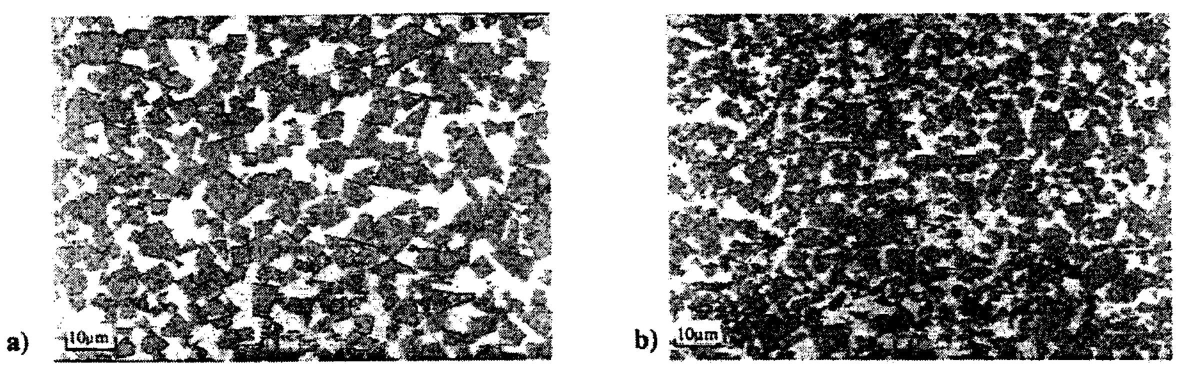


Figure 3. Microstructure of two different hardmetal grades

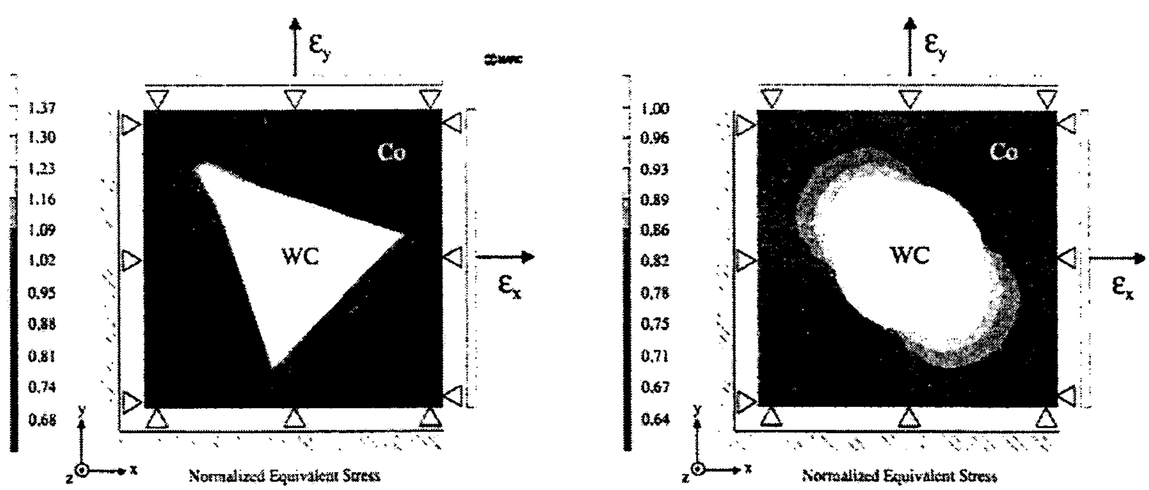


Figure 4. Normalized equivalent stresses illustrated within the binder phase of two different microstructures.

A comparison of Figure 4a and 4b makes it clear that the equivalent stresses in the binder phase at the edges of the triangle are significantly higher than at the grain boundaries of round WC grain.

EXPERIMENTAL PROCEDURE

Based on our experience and references in the literature [6, 7], the following powder batch compositions were used:

A: 12μm *HTC WC-77.5w/oCo-14w/oNi-7w/oCr-1.5w/o

B: 12μm *HTC WC-74w/oCo-15w/oNi-8.6w/oCr-2.4w/o C: 8μm *HTC WC-80w/oW-2w/oCo-11w/oNi-5.5w/oCr-1.5w/o

D: 8μm *HTC WC-74w/oW-3w/oCo-14w/oNi-7w/oCr-2w/o

All grades have a Co:Ni ratio of about 2:1 and incorporate minor additions of Cr. These compositions were chosen with the intent of minimizing intermetallic phases and carbides other than WC in the binder after sintering. It was also necessary to adjust the carbon level for each grade to insure the desired hardmetal properties.

Lab testing of each grade was started by making 10 kg batches of powder in small ball mills using hardmetal balls in an organic fluid. The combination of materials and soft milling conditions was chosen to minimize the comminution of the WC particles in order to obtain rounded grains in the sintered structure.

Also production batches of grade C and D were made in our attrition mill. In order to achieve the same soft milling obtained in the lab ball mill, the attrition milling conditions were varied from normal production practice. This involved milling with both 9mm and 15mm diameter media, as well as varying the milling time and powder charge.

RESULTS AND DISCUSSION

Optimum properties of the hardmetal grades occur at C levels high enough to avoid the formation of h phase and low enough to avoid free C in the sintered structure. This so-called "carbon window" for a grade can be experimentally determined by systematically adding either C or W powders to grade powder by dry mixing, sintering the mixtures and observing the effect on magnetic saturation, density and microstructure of the sintered parts. This procedure was followed for grade A. Density and magnetic saturation data measured on the sintered parts are plotted in Figure 5. The data show that the "carbon window" is about 0.22% C for grade A.

** HTC = High Temperature Carburized*

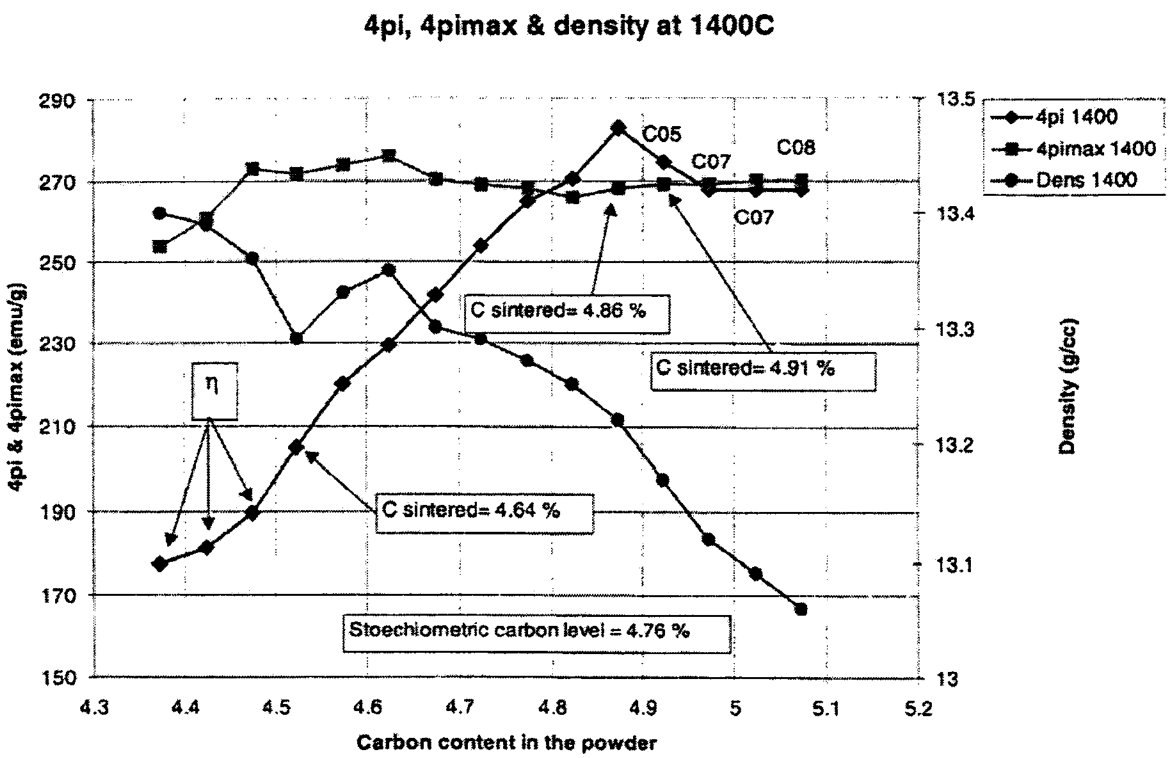


Figure 5.Magnetic saturation and density after sintering versus carbon content in the powder of grade A

The microstructure of grade B, which has a relatively high Cr content, is shown Figure 6a. Note that the WC grains tend to have an angular morphology similar to what is found in straight Co binder grades, the carbon content is on the upper level of the carbon window.

This condition was altered by dry mixing 2% W metal powder to the powder mix of grade B and sintering the samples under the same conditions. The resulting sintered microstructure, seen in Figure 6b, shows a higher proportion of rounded WC grains than is observed in Figure 6a. Also there was no h phase detected in the microstructure indicating the mixture is still within the "carbon window". This result demonstrates that the rounded WC grain morphology is achieved at low C levels within the "carbon window".

In addition two versions of grade C were produced by milling in the attrition mill. The first version was milled with 9mm balls and the second with 15mm balls. The sintered microstructures are shown in Figure 7.

Both materials have microstructures with rounded WC grains however the average grain size is larger for the batch milled with the 15mm balls. Since larger WC grains produce higher toughness it was decided to use only the 15mm balls for the production of roll rings. To validate the improvement brought about by this development roll rings of grade D were produced for field testing. The microstructure of two production batches of grade D rolls produced in the attrition mill with 15mm balls is shown in Figure 8.

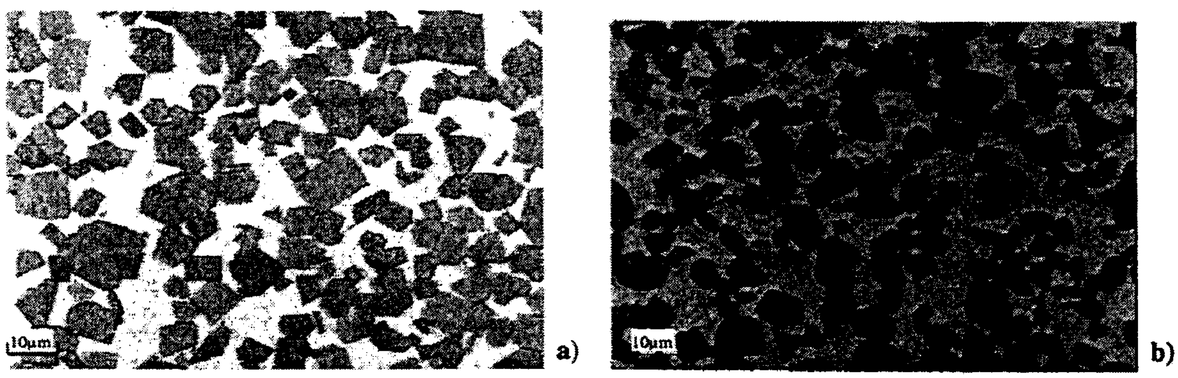


Figure 6. a) Microstructure of grade B with maximum carbon content
b) Microstructure of grade B (undercarburized)

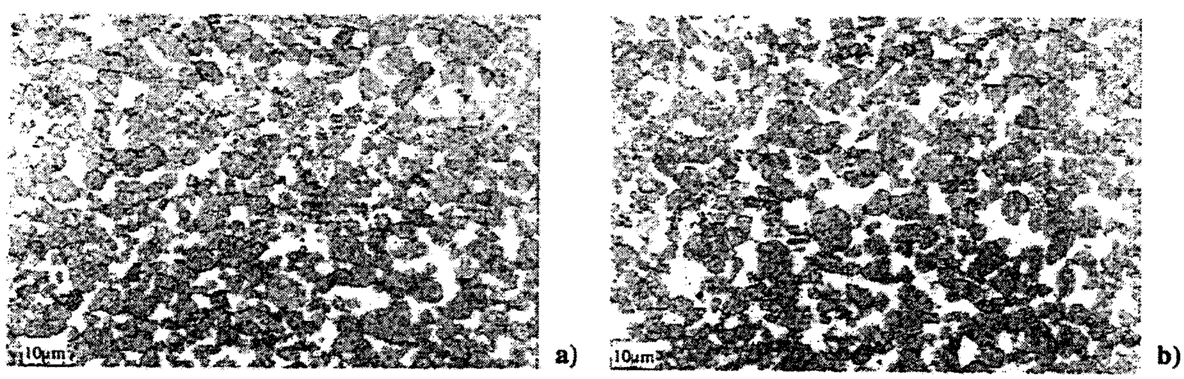


Figure 7. a) Microstructure of grade C milled with 9mm balls
b) Microstructure of grade C milled with 15mm balls

Development of a wear-resistant surface layer for a tool to be used for high-temperature stainless steel rolling

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Abstract: A new method for a tool surface reinforcing coating was presented to prolong the tool life for hot stainless steel rolling above 1473 K. It is basically by welding a Co-based matrix powder mixed with an NbC powder on the surface of a medium-carbon steel using plasma transferred arc (PTA) welding technology. The new tool covers the region where the PTA welded tool for hot stainless steel rolling reinforced by BS 316S12 and NbC powders developed by the present authors fails to show as good a performance as for the rolling under 1473 K. In the laboratory tests, the new tool showed an excellent performance among the trial combinations of matrix and carbide powders, and its superiority was verified through a test rolling by an elongator in a Mannesmann plug mill line.

Keywords: plasma transferred arc (PTA) welding, seamless pipe, tool, wear, adhesion, galling

1 INTRODUCTION

Among the tools used in plastic metal working, those for hot metal working such as rolls and guides are used under the most severe conditions. The tool life is determined, in general, when the amount of at least one of the types of damage such as galling, wear or cracking reaches the limit. If one such index reaches the limit, the tool has to be changed in order to ensure the product dimension and surface quality. As the production line must be stopped to change the tool, it is preferable for the tool to have a longer life to suppress the increase in the production cost due to this stoppage. Usually, the tools used for rolling stainless steels have a shorter life than those for carbon steels, and as a result the production cost for hot stainless rolling inevitably increases.

In order to overcome this disadvantage, the present authors have developed a new technology to reinforce the tool surface using the plasma transferred arc (PTA) welding [1–3] of a mixed powder of BS 316S12 and NbC and successfully applied it to a Mannesmann plug mill to prolong the plug life by ten times compared with that of the conventional plug for the hot rolling of a seamless stainless tube [4]. An illustration is given in Fig. 1 of the PTA

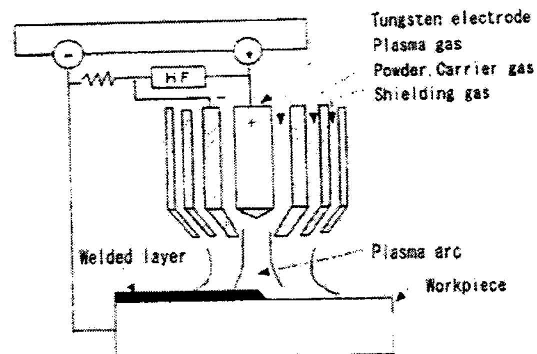

Fig. 1 Illustration of PTA welding

welding, and in Fig. 2 of the Mannesmann plug mill line. If this tool material were automatically applicable to other tools, the benefit would be enormous.

The conventional tool material for the guide shoe of an elongator, the mill immediately upstream to the plug mill, is basically a high-chromium cast steel and the present authors tried to prolong its life by giving it a special heat treatment to granulate a eutectic carbide that is meshy in the cast microstructure [5]. This was successful for carbon steel rolling. However, a different method of reinforcement was necessary to prolong the guide shoe life when rolling stainless steel. In looking for a new method, there are two points to be taken into account as follows:

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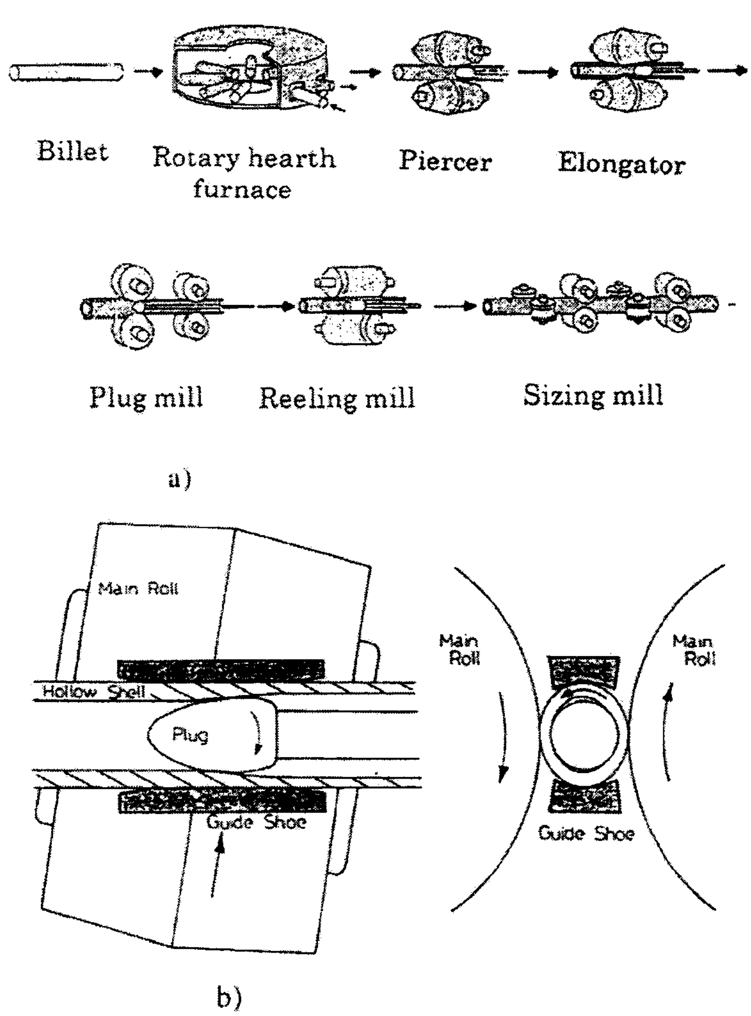

Fig. 2 Illustrations of (a) the Mannesmann plug mill line and (b) elongator rolling

1. As stainless steel has a much higher flow stress at high temperatures than carbon steel does, the wear on the tool surface tends to become greater when rolling a stainless steel shell.
2. As the thickness of the scale layer on the surface of stainless steel is much thinner than that of carbon steel, it is easier when rolling the stainless steel shell for the metal to contact the tool surface under a local breakage in the scale layer.

The same PTA reinforcement technology on the plug mill plug was applied to the guide shoe of the elongator. However, the rolling temperature of the elongator is about 100 K higher than that of the plug mill, and the performance of the new guide shoe was better than that of a conventional guide shoe, but it did not reach the expected level. Adhesion decreased on the carbide-reinforced tool, but the wear did not decrease dramatically. Close observation showed that, between the two important factors, the increase in the resistance against adhesion and galling is achievable by reinforcing the tool by carbide, but a new method must be found to increase the wear resistance of the matrix.

In order to improve the performance of the PTA-welded guide shoe, various combinations of powders of the matrix and the carbide were tried in the laboratory. The final solution of a combination of a Co-based matrix and NbC was found to be the best, and the validity was checked on the guide shoe of the elongator in the production line.

2 APPLICABILITY OF THE CONVENTIONAL PTA WELDING TECHNOLOGY

An investigation was carried out on the applicability of the conventional PTA reinforcing technology for the guide

shoe surface. A mixed powder of NbC and BS 316S12 was welded on to the surface of a guide shoe made of a medium-carbon steel. The surface was then finished by grinding to ensure 3 mm thickness of the welded portion, and a heat treatment was applied to make a thin scale layer on the surface. These procedures were exactly the same as for the plug mill plug [1]. A comparison was made on the performances of the new and the conventional guide shoes. The rolling conditions and the chemical compositions of the guide shoe are shown in Table 1 and Table 2 respectively. After rolling the specified number of stainless steel BS 304S15 shells, the guide shoe was taken off the line and the damage was first observed on the surface. The results are shown in Fig. 3.

In order to achieve the required shell diameter after rolling by the elongator, the wear track after rolling the stainless steel shells is too wide and too deep, and it is hard to ensure the long life of the tool. Close observation of the two worn surfaces showed that the PTA-welded tool prevents the occurrence of macroscopic galling, but no marked improvement in the wear resistance is obtainable. The latter result is totally different from that obtained in the case of the plug mill plug. The reason for this may be the difference in the rolling temperature. The shell temperature is about 100 K higher at the elongator than at the plug mill.

Test pieces were then sectioned from the used guide shoe and observations were made on the microstructures in the vicinity of the contacting surface by optical microscopy. The sectioned plane was polished and etched by Nital (3% HNO_3–97% ethyl alcohol) for preparation for optical microscopy. An example of the surface observation results is shown in Fig. 4. It is important to note that, although there is typical galling on the conventional tool surface, there are very few small adhesions on the PTA-welded surface. Therefore, it may be concluded that the projected particles of NbC prevent adhesion of the shell material to the matrix.

The results suggest that the fundamental philosophy of tool surface reinforcement by PTA welding may be valid, and the next step to be taken is the reinforcement against wear of the matrix.

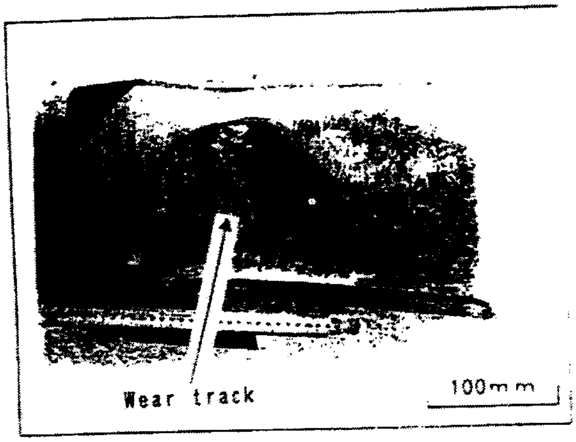

Fig. 3 Guide shoe surface after use

Table 1 Rolling conditions of the elongator

Billet	
Material	BS 304S15
Diameter	236 mm
Length	3000 mm
Rotary hearth furnace	
Target billet temperature	1503 K
Elongator	
Thickness of hollow shell	29.8 mm
Plug diameter	209 mm
Thickness of rolled shell	16.2 mm
Sizing mill	
Rolling diameter	254.8 mm
Rolling thickness	13.5 mm
Rolling length	12 700 mm

Table 2 Chemical composition of the conventional guide shoe and the composition of the powders of the PTA

Conventional guide shoe	
Material	25Cr-Ni
Chemical composition (mass %)	C, 1.18; Si, 0.41; Mn, 0.40; P, 0.019; S, 0.035; Cr, 25.71; Ni, 2.96
PTA-welded guide shoe	
Matrix powder (vol %)	50 BS 316S12
Carbide powder (vol %)	50 NbC

3 LABORATORY TESTS

In order to select an optimum combination of the powders, three kinds of carbide powder (NbC, WC and Cr_3C_2) and three kinds of matrix powder (BS 316S12, Ni-based alloy and Co-based alloy) were tested.

3.1 Experiments

The combinations of powders are shown in Table 3. Co-based matrix powder was chosen as it is generally understood that Co-based alloys have a high strength at high temperatures [3], and it was assumed that the wear resistance might increase on using a Co-based matrix.

An average diameter of 100 μm was selected for the carbide powder following the conclusion of the previous paper on the PTA reinforcement of a plug surface [1], namely that, if the powder is finer, it will be blown away owing to the pressure of the plasma and, if it is larger, difficulty arises in smooth PTA welding.

The wear test was carried out in the following manner using equipment for the wear test illustrated in Fig. 5. Test pieces were sectioned from the conventional guide shoe, the chemical compositions of which are given in Table 2.

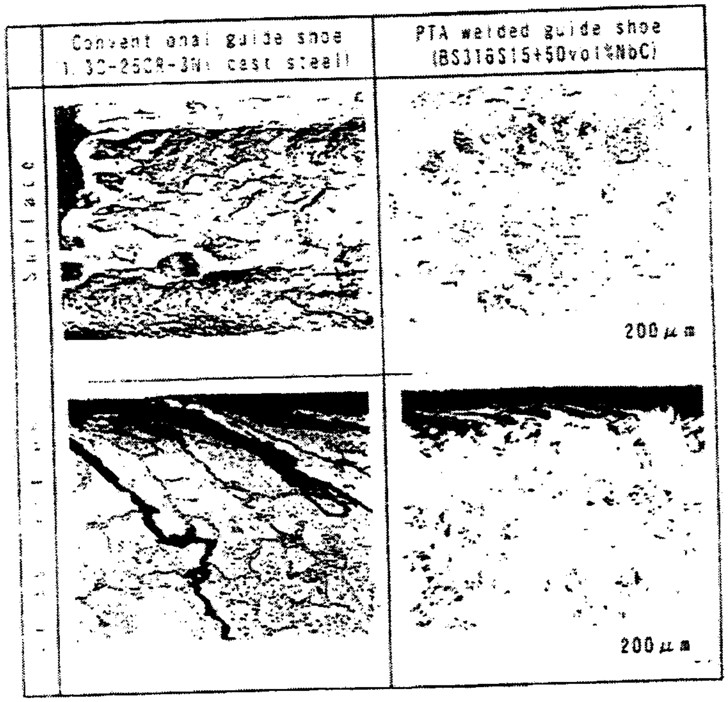

Fig. 4 Comparisons of the observed guide shoe surfaces after use

Table 3 Powders used for the trial tests in the laboratory

Matrix powder	Stainless steel (BS316S12)
	Ni-based alloy (Alloy 625)
	Co-based alloy (Stellite 6)
Carbide powder	NbC
	WC
	Cr_3C_2
Average powder size	100 μm

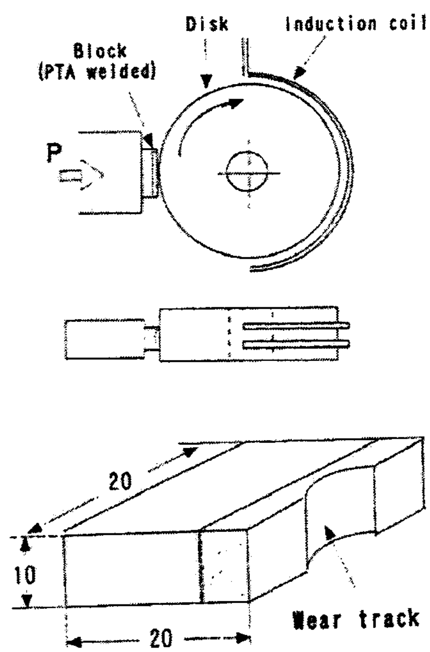

Fig. 5 Illustration of the wear test

and the combined powder of carbide and matrix was welded by PTA on the specimen. The welded surface was given a smooth finish by machining and then subjected to the wear test. The testing conditions are given in Table 4 together with the dimensions of the specimen. A comparison is shown in Fig. 6 of the PTA-welded microstructures by optical microscopy.

After the test, the specimen was taken out of the equipment and then the worn surface was observed. The amount of wear was then measured; the worn surface was observed to check the galling damage. As an index of the high-temperature strength of the matrices, the hardness at high temperatures was measured by the Brinell testing method on the PTA-welded specimens made by using only matrix powders.

3.2 Results

A comparison of the worn surfaces is shown in Fig. 7. Heavy galling was observed on the conventional tool surface whereas very little galling was observed on any of the PTA-welded tool surfaces. It is noteworthy that the number of rotations of the specimen for the wear test was lower for the conventional tool than for the PTA-welded

Table 4 Conditions of the wear test

Block	
Thickness	10 mm
Width	20 mm
Length	20 mm
Material	PTA-welded layer
Disc	
Diameter	100 mm
Thickness	30 mm
Material	BS 304S15
Temperature	1373 K
Applied load	980 N
Sliding speed	1 m/s
Sliding distance	600 m
Lubrication	No lubricant (water spraying for cooling the block)

tools. It is suggested that the PTA-welded tool, regardless of the combination of the powders, may be superior in rolling a high-temperature stainless steel as far as galling is concerned.

The other important fact to note is that the various combinations of the matrix and carbide powders have different wear resistances. The result is shown in Fig. 8. A comparison is also given of the high-temperature hardness, which is an index of the high-temperature strength, for the PTA-welded surfaces made of only the pure matrix powders. It is clear that the combination of the Co-based matrix powder and the NbC powder shows the best performance as far as wear resistance is concerned. This shows that the Co-based alloy matrix may demonstrate a better performance in operation than BS 316S12 when rolling stainless steel at a high temperature above 1473 K.

It may be concluded that the projection of carbide particles protects the tool surface from adhesion or galling even if the rolling temperature is above 1473 K. It may also be concluded that, the higher the strength of the matrix at high temperatures, the better the resistance against wear becomes.

4 VALIDITY CHECK ON THE PRODUCTION LINE

In order to check the validity of the conclusion of the laboratory test, the Co-based matrix powder and the NbC powder, of volume fractions 50 and 50 per cent respectively, were welded by the PTA technology on to an elongator guide shoe made of a medium-carbon steel. The welded surface was finished by grinding to a welded layer thickness of 3 mm. Under the same conditions as in Table 1, the same number of BS 304S15 shells were rolled. The guide shoe was then taken off the mill to observe the

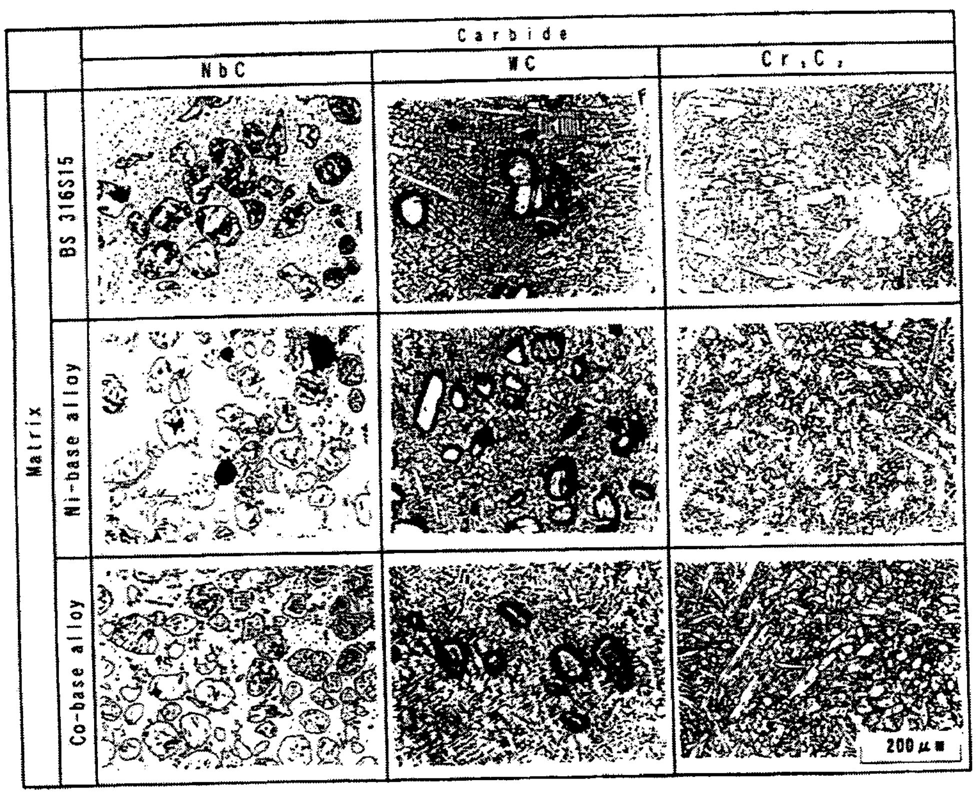

Fig. 6 Comparison of PTA-welded microstructures

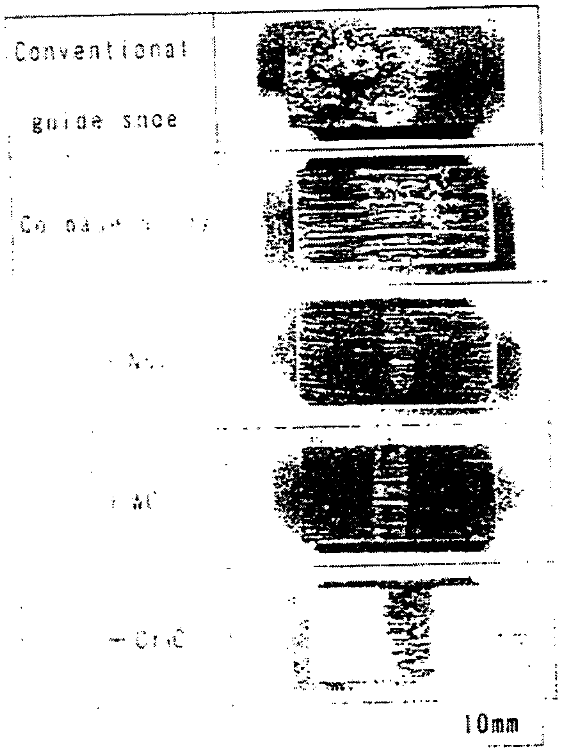

Fig. 7 Comparison of worn surfaces after the laboratory tests

performance of the new tool. Comparisons of galling, adhesion and wear are given in Fig. 9 between the conventional and the new guide shoes.

It is clear that the new guide shoe is far superior to the conventional guide shoe, and very few small adhesions were observed on the surface, whereas almost immediately galling appeared on the conventional guide shoe.

However, cracks were observed in the PTA-welded layer and a specimen was sectioned from the guide shoe to investigate the depth. The sectioned surface was polished and etched by Nital in the same manner as in the laboratory tests. An example of the results obtained by optical spectroscopy is shown in Fig. 10.

It is important to note that the crack tip stopped on the boundary between the PTA-welded layer and the base metal and did not propagate over the boundary. This result is the same as the harmless cracks observed by the present authors on the PTA-welded plug for the plug mill rolling. Although the temperature of the shell for the plug mill was lower than that of the elongator and the matrix powder for the plug was BS 316S12, which is different from the present Co-based alloy, the behaviour of the crack tip was the same.

It was, therefore, assumed that the present cracks might also be harmless when they do not propagate over the boundary, and other PTA-welded guide shoes were made in order to check the life. The rolling condition was the same as in Table 1 and the results are compared with those for the conventional guide shoes in Table 5. There was no

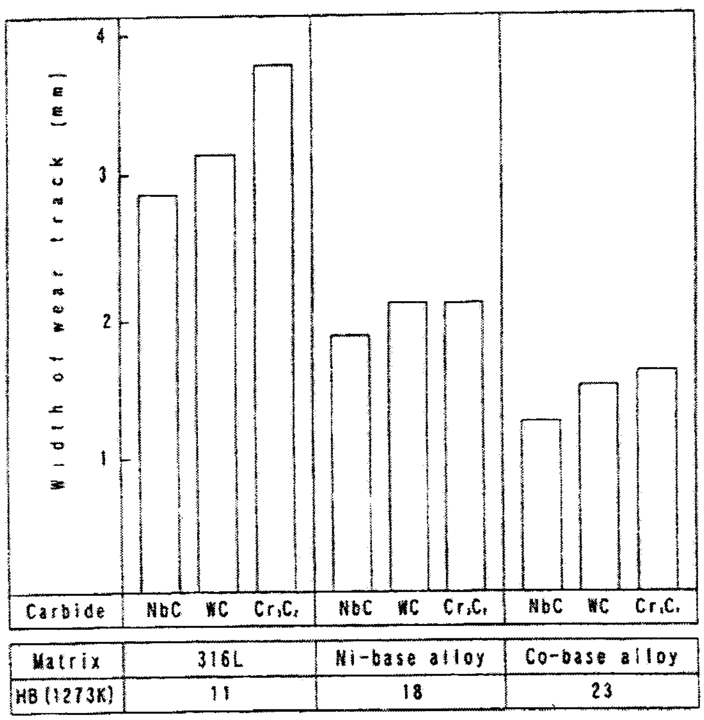

Fig. 8 Comparison of the wear resistances of the PTA-welded tool surfaces

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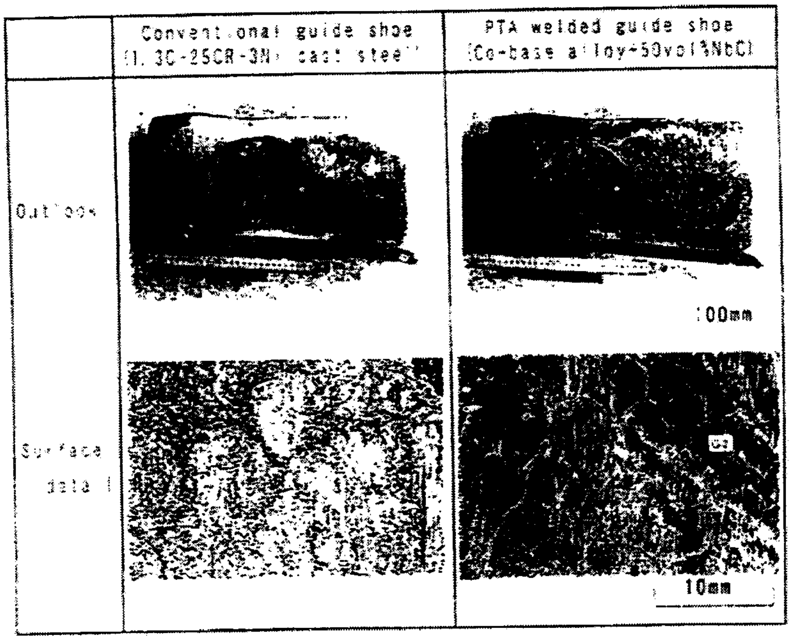

Fig. 9 Comparisons of the performance of the conventional and the proposed guide shoes

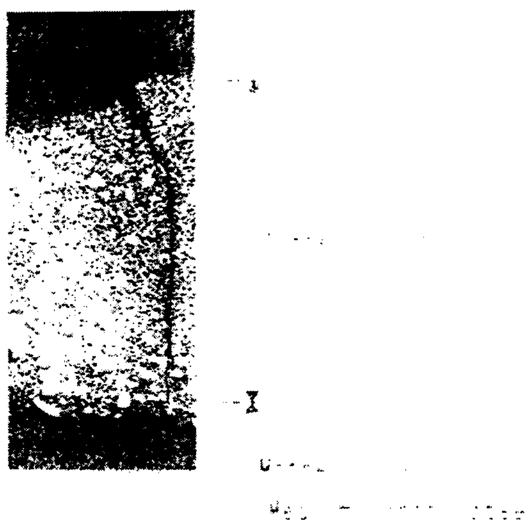

Fig. 10 Cracks observed on the PTA-welded surface

Table 5 Comparison between the tool lives of the conventional and the PTA guide shoe

	Conventional guide shoe	PTA-welded guide shoe
Tool life	21 passes	60 passes
Maximum wear depth	5.3 mm	5.4 mm
Wear rate	0.25 mm/pass	0.09 mm/pass

propagation of cracks over the boundary to cause fatal damage to the tool, nor any fatal damage to the rolled shell, which may prove the superiority of the PTA-welded guide shoe.

5 CONCLUSIONS

1. A trial application was made of the technology using a PTA-welding method to reinforce a tool surface for hot stainless steel rolling at a temperature above 1473 K.
2. A straightforward application of the successful combination of PTA powders consisting of 50% BS 316S12 and 50% NbC for the plug used for the rolling at 1273 K suppressed the galling but failed to extend the tool life because of the wear. COATING COST 1/3 ROLLER
3. Laboratory experiments showed that projected carbide particles of any kind used in the experiments prevent the occurrence of adhesion regardless of the testing temperature but, of the trial carbides, NbC showed the best performance.
4. Regarding the suppression of wear, Co-based alloy showed the best performance of the trial matrix powders. In other words, the increase in the high-temperature strength of the matrix may be crucial in increasing the wear resistance at high temperatures.
5. The validity of the results obtained in the laboratory tests was confirmed by applying it to a guide shoe for the hot stainless steel rolling of an elongator in the Mannesmann plug mill line.

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